

A Contribution to the Study of Liquid Mixtures of Constant Boiling-point

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHNS HOPKINS UNIVERSITY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

—BY—

GARNETT RYLAND

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ACKNOWLEDGMENT.

This investigation was pursued under the supervision of Professor Ira Remsen.

I wish to express to him, together with Professors Morse, Renouf, and Ames, my appreciation of their instruction, counsel, and kindness.

A CONTRIBUTION TO THE STUDY OF LIQUID MIXTURES OF CONSTANT BOILING-POINT.

INTRODUCTION.

In the course of certain investigations a mixture of methyl alcohol and benzene was subjected to a fractional distillation, when it was observed that the larger part boiled like a homogeneous liquid at 57° – 58° , and could not be separated by repeated distillation with a Hempel tube. By making trial mixtures it was found that, mixed in certain definite proportions, methyl alcohol and benzene will boil to the last drop at 57° – 57.5° , under atmospheric pressure. If there be present an excess of either of the constituents, the constant boiling mixture and this excess are separated by fractional distillation. As roughly determined the proper ratio seemed approximately $3\text{CH}_3\text{O} : 2\text{C}_6\text{H}_6$ (38.1 parts of alcohol to 61.9 parts of benzene, by weight).

On examination of literature no such observation of this mixture could be found, though several similar phenomena are on record.

HISTORICAL SKETCH.

1. H. E. Roscoe¹ investigated certain aqueous acids of constant boiling-point, which had been regarded as definite hydrates, and found that the proportions of water and acid were not those required by any simple molecular ratio, nor did the composition remain the same when the pressure varied.

Aqueous nitric acid, when distilled under a pressure of 735 mm., always gave a residue which boiled at 120.5° , and contained 68 per cent. of pure acid. Distilled under 75 mm. pressure, the per cent. of pure acid was 66.7; and under 1260 mm., became 68.8.

¹ "On the Composition of Aqueous Acids of Constant Boiling-point." J. Chem. Soc., **13**, 146 (1861), and **15**, 270 (1862).

Aqueous solutions of hydrochloric, hydrobromic, and hydriodic acids gave similar phenomena, only in these cases the per cent. of acid increased as temperature and pressure decreased. Hydrofluoric acid resembled nitric acid in all respects.

Aqueous formic acid containing 77.5 per cent. of pure acid (boiling-point 101.1°), boiled at the fixed temperature of 107.1° , under 760 mm. pressure, the proportion of acid increasing with the pressure.

Aqueous perchloric acid¹ gave a residue which boiled constant at 203° , under atmospheric pressure, and contained 71.6 per cent. pure acid.

2. Alexander Bauer² found that a mixture of ethylene bromide (boiling-point 129°) and propylene bromide (boiling-point 141°) in equivalent amounts, was distilled at 134° , and could not be separated by fractionation.

3. J. A. Wanklyn³ called attention to the fact that in the distillation of a mixture of liquids the proportions in which the constituents pass over depend not merely on their relative quantity and on their respective vapor-tensions at the temperature of ebullition, but also upon their mutual adhesion and on the density of their vapors.

On distilling a mixture of 18 grams of methyl alcohol (boiling-point 66°) and 17 grams of ethyl iodide (boiling-point 72°), the first third of the distillate contained a greater amount of the less volatile than of the more volatile liquid.

4. Berthelot⁴ stated that a mixture of 91 parts carbon disulphide (boiling-point 48°) and 9 parts alcohol (boiling-point 78°), by weight, boils at 43° – 44° , remaining at this temperature from the beginning until the end of the distillation. A mixture of this composition is separated by fractional distillation from an excess of either of its components.

He found the explanation of this phenomenon in essentially

¹ "On Perchloric Acid and its Hydrates." *Proc. Roy. Soc.*, **11**, 493 (1862).

² "Ueber eine merkwürdige Erscheinung bei der Destillation eines Gemenges von Bromäthylen und Brompropylen." *Ann. Supp.*-band, **I** (1861), p. 250.

³ "Ueber die Destillation von Gemischen; ein Beitrag zur Theorie der fractionirten Destillation." *Ann. Chem. (Liebig)*, **28**, 328 (1863).

⁴ "Sur la Distillation des Liquides Melangés." *Ann. chim. phys.* [4], **1**, 384 (1864).

physical ideas. If a mixture of two liquids which do not exert any reciprocal action be boiled, both will be volatilized at that temperature at which their united vapor-tensions equal the atmospheric pressure, and in the same ratio by weight as that of the products of their actual vapor-tensions by their vapor-densities respectively. So if the carbon disulphide and alcohol preserved their theoretical vapor-tensions, they would be distilled at about 40° in the proportions of 88.5 parts of carbon disulphide and 11.5 parts of alcohol. But the two liquids exert influence upon each other, as is shown by their mutual solution and by the diminution of the sum of the tensions of their vapors. This influence tends to diminish the individual vapor-tension of each of the liquids, following an unknown law.

5. Ed. Linnemann¹ records three hydrates of isopropyl alcohol (boiling-point 83° – 84° , 739 mm.); $3C_3H_8O + 2H_2O$, formed when aqueous propyl alcohol is distilled on the water-bath, boils at 78° – 80° (738 mm.), specific gravity, 0.832, at 15; $2C_3H_8O + H_2O$, formed by dehydration with potassium carbonate, boils at 80° ; $3C_3H_8O + H_2O$, formed by distilling from anhydrous copper sulphate, boils at 81° , specific gravity, 0.800.

6. T. E. Thorpe² found that a mixture of 1 part methyl alcohol and 3.6 parts carbon tetrachloride boils like a homogeneous liquid about 10° lower than methyl alcohol, the more volatile of the two liquids. Calculation shows that this ratio is almost identical with that obtained by multiplying the vapor-tensions of the two liquids at the temperature of the boiling-point (55.7°) by their respective vapor-densities.

7. D. Konowalow³ investigated the known mixture of propyl alcohol (boiling-point 97.4°) and water in the ratio of about 77 : 23 parts, which boils at 85° – 85.5° . To this composition corresponded the maximum of the curve, whose ab-

¹ "Untersuchung über die Beziehungen des isopropyl Alcohols zum propyl Glycol und zum Glycerin." *Ann. Chem. (Liebig)*, **136**, 40 (1865).

² "A Contribution to the Theory of Fractional Distillation." *J. Chem. Soc.*, **35**, 544 (1879).

³ "Ueber die Dampfspannungen der Flüssigkeitsgemische." *Wied. Ann.*, **14**, 34 (1881).

scissae are percentage quantities and ordinates pressures, representing the vapor-tension of the mixture at a specific temperature.

He found also that a 25 per cent. solution of butyric acid (boiling-point 163°) in water boiled constant at 99.5° . Both of these mixtures change their respective proportions on change of the pressure and temperature of distillation.

8. Ramsay and Young¹ agreed with Konowalow that the mixture of propyl alcohol and water, thought by Chancel to be $C_3H_7O + H_2O$, which distils to the last drop at 87.5° (738 mm.), is not a definite hydrate. The normal composition of the mixture (71.46 per cent. alcohol to 28.54 per cent. water) varied with the pressure under which it was distilled.

APPARATUS FOR DISTILLATION UNDER REDUCED PRESSURE.

Mixtures of methyl alcohol and benzene were distilled under different pressures, and the relative amounts of the two liquids contained in the constant boiling portion of the distillates were determined.

The apparatus used to effect fractional distillation, under reduced pressure, was arranged as follows: ²

A 250 cc. separatory funnel was used as a receiver. This was closed with a two-hole rubber stopper, through which passed the adapter and a branched tube, the latter connecting with the manometer, the exhaust, and the pressure regulator. The last was a glass tube about 800 mm. in length and 20 mm. in diameter, filled to the necessary height with mercury, and closed at the top with a two-hole rubber stopper through which passed a short and a long piece of small glass tubing. The first connected with the receiver and the latter extended below the surface of the mercury a distance corresponding to the desired diminution of pressure. By this means the pressure could easily be kept constant within 10 mm. without interrupting the course of distillation. Successive fractions were drawn off from the funnel into an exhausted receiver, through whose stopper the stem of the funnel passed.

¹ "Note on the Mixture of Propyl Alcohol and Water." Abs. Proc. Chem. Soc., 1888-1889, p. 101.

² My thanks are due to Dr. E. E. Reid, of this laboratory, for his kind assistance in designing and constructing this apparatus.

The liquid was distilled from a bulb provided with an additional side tube, connected by rubber and a pinch-cock with a small funnel, into which successive fractions were poured. With caution these could be introduced without diminishing the exhaustion.

METHYL ALCOHOL AND BENZENE.

Method of Analysis.—The distillates were analyzed by the following method :

30–40 cc. of the fraction boiling at a constant temperature were measured off into a burette and a definite proportion of water added. It was found that when alcohol constituted 30–40 per cent. of the distillate the water added should be one-third of the volume of the sample. The burette was closed, shaken vigorously, and allowed to stand until the liquid within separated into two sharply divided layers of benzene and aqueous alcohol solution. The volume of benzene could then be read off and its volume ratio to the alcohol converted into the weight ratio by determining the specific gravity of each liquid.¹

A series of six test determinations of known mixtures gave the following results for the per cent. of benzene by volume :

	Per cent. of benzene.					
	I.	II.	III.	IV.	V.	VI.
Calculated	58.8	59.5	59.5	60.0	64.0	64.0
Found	58.0	59.4	59.8	60.5	63.5	64.3

Results.—Methyl alcohol (distilled from lime at 64.5° – 65°)² and commercial benzene (redistilled at 79° – 79.5°) were mixed in the proportions by weight, and distilled at the pressures given below. The constant boiling portions analyzed were separated from the excess of either constituent by three fractional distillations in each case.

¹ The difference between the actual specific gravity of a solution of benzene in methyl or ethyl alcohol and that calculated from the specific gravities of the individual liquids was found by Paterno and Montemartini [Gazz. chim. ital., **24**, II, p. 179 (1894)], to be so small (1 or 2 in the third decimal place) that it may be disregarded in this method of determination.

² The same thermometer was used throughout this and all succeeding investigations. It had been carefully tested, compared with two standard thermometers, and corrected. Whenever the pressure under which a liquid was distilled is not stated, it was approximately 760 mm.

	Ratio of alcohol to benzene (by weight) in mixture distilled.	Pressure. mm.	Boiling-point of fraction analyzed.	Per cent. of alcohol found.	Per cent. of benzene found.	Ratio of products of vapor-tension by vapor-density. ¹
I.	38 : 62	770	58°	38.4	61.6	At 60°, 37.8 : 62.2
II.	38 : 62	760	57.5-58°	39.0	61.0	
III.	37 : 63	400	40°	36.8	63.2	At 40°, 35.2 : 64.8
IV.	36 : 64	392	39.5°	35.7	64.3	
V.	41 : 59	223	25°	33.2	66.8	At 25°, 33.2 : 66.8
VI.	34 : 66	223	25°	33.1	66.9	

ETHYL ALCOHOL AND BENZENE.

Mixtures of ethyl alcohol (distilled from anhydrous copper sulphate at 77.5°-78°) and benzene (79°-79.5°) were investigated, and it was found that a mixture containing about 32 per cent. of alcohol was distilled to the last drop at 67°-68°.

The results of the analysis of distillates under various pressures, obtained as in the case of methyl alcohol and benzene, are as follows :

	Ratio of alcohol to benzene (by weight) in mixture distilled.	Pressure. mm.	Boiling-point of fraction analyzed.	Per cent. of alcohol found.	Per cent. of benzene found.	$\frac{v. t. \times v. d. \text{ of alcohol}}{v. t. \times v. d. \text{ of benzene}}$
I.	33 : 67	769	67°-68°	31.4	68.6	At 67.5°, 36.3 : 63.7
II.	33 : 67	763	67°-68°	32.3	67.7	
III.	33 : 67	421	50°-51°	28.2	71.8	At 50°, 32.3 : 67.7
IV.	28 : 72	423	50°-51°	27.6	72.4	
V.	28 : 72	241	34.5°-35.5°	23.3	76.7	At 35°, 28.9 : 78.1
VI.	23 : 77	243	34.5°-35.5°	23.4	76.6	

To determine the percentage composition of the distillates, 40 cc. were shaken with 50-60 cc. of water.

Twelve analyses of known mixtures gave the following results for the per cent. of benzene by volume :

¹ See Berthelot, page 6; and Thorpe, page 7. The values for vapor-tensions throughout these investigations were taken from Landolt and Börnstein's tables, Regnault's values preferred.

	I.	II.	III.	IV.	V.	VI.
Calculated	60.0	60.0	60.0	65.0	65.0	65.0
Found	59.9	59.5	62.2	65.2	64.8	65.0
	VII.	VIII.	IX.	X.	XI.	XII.
Calculated	65.0	70.0	70.0	70.0	75.0	75.0
Found	66.2	70.1	69.8	70.0	75.0	75.1

GENERAL INVESTIGATION OF THE BOILING-POINTS OF
BINARY MIXTURES OF LIQUIDS MUTUALLY SOLUBLE
IN ALL PROPORTIONS.

All liquids boiling below 170° that were at hand were purified; and each was mixed with every other whose boiling-point was within 30° – 40° of its own, and the mixture distilled. When a constant boiling mixture was found, the ratio of its constituents was determined as nearly as possible by repeated mixing in various proportions and careful distillation until that ratio was discovered for which the whole mixture distilled most nearly within one degree. A volume of 10–15 cc. was found adequate for each trial mixture distilled.

The ratio of the products of the respective vapor-densities and vapor-tensions at a temperature near that of constant boiling was calculated whenever the necessary data were known, and is given below as the "theoretical ratio."

1. Methyl alcohol (64.5° – 65°) and ethyl bromide (37.5° – 38.5°) are distilled at 35° – 36° (765 mm.) in the approximate ratio of 5 : 95 parts by weight. Theoretical ratio at 35° , 9 : 91 parts by weight.

2. Methyl alcohol and chloroform (60° – 61°) at 53.5° – 54.5° (765 mm.); ratio, 12 : 88. Theoretical ratio at 55° , 17 : 83.

3. Methyl alcohol and methyl acetate (55.5° – 56.5°) at 53.5° – 54.5° (760 mm.); ratio, 18 : 82.

4. Methyl alcohol and ethyl iodide¹ (72.3° – 72.5°) at 54.5° – 55.5° (770 mm.); ratio, 17 : 83. Theoretical ratio at 55° , 19 : 81.

5. Methyl alcohol and ethyl acetate (75.5° – 76.5°) at 61.7° – 62.5° (757 mm.); ratio, 47 : 53.

6. Methyl alcohol and benzene. (See p. 10.)

¹ See Wanklyn, page 6.

7. Methyl alcohol and isobutyl iodide (118° – 119°) at 63.5° – 64.5° (760 mm.). The ratio of 70 : 30 parts by weight gave an excess of alcohol. In this and all succeeding distillations of isobutyl iodide mixtures, the formation of tar made a close determination of the proportions impossible.

Methyl alcohol is separated by fractional distillation from ether (34.5° – 35.5°), acetone (56° – 57°), and toluene (108.5° – 109.3°).

8. Ethyl alcohol (77.5° – 78°) and ethyl bromide (37.5° – 38.5°) at 36.5° – 37.5° (762 mm.). The theoretical ratio at 37.5° is 6.6 : 93.4. The actual per cent. of alcohol seemed to be about half of the theoretical, but could not be more closely determined.

9. Ethyl alcohol and carbon disulphide¹ (45.5° – 46°) at 41.5° – 42.5° (755 mm.); ratio, 9 : 91, verified. Theoretical ratio at 43° – 44° , 11.4 : 88.6.

10. Ethyl alcohol and chloroform (60° – 61°) at 58.5° – 59.5° (759 mm.); ratio, 6 : 94. Theoretical ratio at 60° , 15.6 : 84.4.

11. Ethyl alcohol and ethyl iodide (71.5° – 72.5°) at 62.5° – 63.5° (761 mm.); ratio, 14 : 86. Theoretical ratio at 60° , 17.4 : 82.6.

12. Ethyl alcohol and ethyl acetate (75.5° – 76.5°) at 71° – 72° (765 mm.); ratio, 31 : 69.

13. Ethyl alcohol and benzene. (See p. 10.)

14. Ethyl alcohol and isobutyl iodide (118° – 119°) at 76.5° – 77.5° (760 mm.); approximate ratio, 70 : 30.

Ethyl alcohol is separated from propyl alcohol (97.5°) and toluene (108.7° – 109.3°).

15. Isopropyl alcohol (81° – 82°) and carbon disulphide (45.5° – 46°) at 43.5° – 44.5° (761 mm.); ratio, 9 : 91.

16. Isopropyl alcohol and ethyl iodide (71.5° – 72.5°) at 65.5° – 66.5° (764 mm.); ratio, 13 : 87.

17. Isopropyl alcohol and ethyl acetate (75.5° – 76.5°) at 74° – 75° (770 mm.); approximate ratio, 26 : 74.

18. Isopropyl alcohol and benzene (79° – 79.5°) at 71° – 72° (758 mm.); ratio, 30 : 70.

¹See Berthelot, page 6.

19. Isopropyl alcohol and water at 78.5° – 79.5° (768 mm.); ratio, 89 : 11.¹

20. Isopropyl alcohol and isobutyl iodide (118° – 119°) at 81° – 82° (761 mm.); approximate ratio, 70 : 30.

Isopropyl alcohol is separated from chloroform (60° – 61°) and toluene (108.7° – 109.3°).

21. Normal propyl alcohol (95.7°) and ethyl iodide (72.3° – 72.5°) at 69.5° – 70.5° (768 mm.); approximate ratio, 7 : 93.

22. Propyl alcohol and benzene (79° – 79.5°) at 76° – 77° (762 mm.); ratio, 16.5 : 83.5. Theoretical ratio at 80° , 28.5 : 71.5.

23. Propyl alcohol and water at 87° – 87.5° (770 mm.); ratio, 72 : 28.² Theoretical ratio at 87.5° , 79 : 21.

24. Propyl alcohol and toluene (108.7° – 109.3°) at 91° – 92° (765 mm.); ratio, 53 : 47.

25. Propyl alcohol and isobutyl iodide (118° – 119°) at 92.5° – 93.5° (753 mm.); approximate ratio, 45 : 55.

Normal propyl alcohol is separated from ethyl acetate (75.5° – 76.5°) and isobutyl alcohol (105.3° – 106.3°).

26. Isobutyl alcohol (105.3° – 106.3°) and toluene (108.8° – 109.3°) at 100° (764 mm.); ratio, 43 : 57.

27. Isobutyl alcohol and isobutyl iodide (118° – 119°) at 101° – 102° (765 mm.). The ratio of 33 : 67 gave an excess of alcohol.

28. Isobutyl alcohol and ethylene bromide (129° – 130°) at 104.5° – 105.5° (763 mm.); approximate ratio, 62 : 38.

Isobutyl alcohol is separated from ethyl iodide (72.3° – 72.5°), benzene (78.5° – 79°), and metaxylene (136° – 137°).

29. Amyl alcohol (128° – 129°)³ and isobutyl iodide (118° – 119°) at 115° – 116° (765 mm.). The ratio of 20 : 80 gave a slight excess of iodide.

30. Amyl alcohol and ethylene bromide (129° – 130°) at 121° – 122° (760 mm.); ratio, 30 : 70. Ratio of vapor-densities, 32 : 68.

¹ See Linnemann, page 7. The per cent. of water in the compounds $3C_3H_8O.2H_2O$, $2C_3H_8O.H_2O$ and $3C_3H_8O.H_2O$ is 16.7, 13, and 9 per cent. respectively. The alcohol used by me was distilled from lime at 81° – 82° . This case should be investigated further.

² See Konowalow, page 7; and Ramsay and Young, page 8. My determination of the ratio was made before I knew of that found by Ramsay and Young.

³ This was obtained by repeated fractionation from the commercial mixture of amyl alcohols.

31. Amyl alcohol and metaxylene (136° – 137°) at 125° – 126° (760 mm.); ratio, 52:48. Amyl alcohol and paraxylene (137° – 137.5°) at 125° – 126° , in the same ratio; and amyl alcohol and orthoxylene (140° – 141°) at 127° – 128° , with a slightly larger per cent. of alcohol.

Amyl alcohol is separated from toluene (108.8° – 109.3°).

32. Allyl alcohol (95° – 96°) and benzene 79° – 79.5°) at 76° – 77° (760 mm.). The ratio of 20:80 gave a slight excess of alcohol.

33. Allyl alcohol and toluene (108.8° – 109.3°) at 91° – 92° (756 mm.); approximate ratio, 50:50.

34. Acetic acid (117° – 118°) and toluene (108.8° – 109.3°) at 103.5° – 104.5° (761 mm.); ratio, 30:70.

35. Acetic acid and metaxylene (136° – 137°) at 113.5° – 114.5° (761 mm.); ratio, 27:73.

Acetic acid is separated from carbon disulphide (45.5° – 45.7°) and benzene (79° – 79.5°).

36. Butyric acid (159° – 160°) and water at 99° – 99.5° (763 mm.); ratio, 20:80.¹ Theoretical ratio at 100° , 32:68.

37. Butyric acid and brombenzene (152° – 153°) at 147° – 148° (748 mm.); ratio, 19:81.

38. Ether (34.5° – 35.5°) and carbon disulphide (45.5° – 46°) at 34.5° – 35.5° (768 mm.); approximate ratio, 65:35. Theoretical ratio at 35° , 59:41.

Ether is separated from acetone (56° – 57°) and chloroform (60° – 61°). A mixture of ether and ethyl bromide (37.5° – 38.5°) is distilled at the same temperature (35° – 38°) as its constituents.

39. Carbon disulphide (45.5° – 45.7°) and ethyl bromide (37.5° – 38.5°) at 37° – 38° (770 mm.); ratio, 32:68. Theoretical ratio at 37.5° , 35:65.

40. Carbon disulphide and acetone (55.5° – 56.5°) at 38.5° – 39.5° (766 mm.); ratio, 74:26. Theoretical ratio at 40° , 66:34.

41. Carbon disulphide and methyl acetate (55.5° – 56.5°) at 39° – 40° (756 mm.); ratio, 71:29.

¹ See Konowalow, page 8.

42. Carbon disulphide and ethyl acetate (75.5° – 76.5°) at 45.5° – 46.5° (768 mm.); ratio, 92 : 8.

Carbon disulphide is separated from chloroform (60° – 61°), ethyl iodide (71.5° – 72.5°), and benzene (79° – 79.5°).

43. Acetone (55.5° – 56.5°) and methyl acetate (55.5° – 56.5°) in about equal parts are distilled 0.5° below the boiling-point of either.

44. Acetone and ethyl iodide (71.5° – 72.5°) at 55° – 56° (770 mm.); approximate ratio, 60 : 40.

45. Acetone and chloroform (60° – 61°) at 64° – 65° (760 mm.); approximate ratio, 20 : 80.

Acetone is separated from ethyl bromide (37.5° – 38.5°) and ethyl acetate (75.5° – 76.5°).

46. Chloroform (60° – 61°) and methyl acetate (55.5° – 56.5°) at 64° – 65° (760 mm.); approximate ratio, 78 : 22.

Chloroform is separated from ethyl bromide (37.5° – 38.5°), ethyl iodide (71.5° – 72.5°), ethyl acetate (76° – 77°), and benzene (79° – 79.5°).

47. Ethyl iodide (71.5° – 72.5°) and ethyl acetate (75.5° – 76.5°) at 69.5° – 70.5° (762 mm.); approximate ratio, 78 : 22.

48. Ethyl iodide and benzene (79° – 79.5°) at 74° – 75° (758 mm.); approximate ratio, 80 : 20.

Ethyl acetate (75.5° – 76.5°) is separated from benzene (79° – 79.5°).

Isobutyl iodide (118° – 119°) is separated from toluene (108.7° – 109.3°).

Acetone (55.5° – 56.5°) and benzene (79° – 79.5°) in the ratio of 5 : 1 approximately, showed a tendency to gather at 57° – 58° , this fraction constantly increasing throughout the course of repeated distillations. But the proportions could not be found for which all of the mixture would boil at this point, as in every case there were small fractions from 57° to 79° .

Ethylene bromide (129° – 130°) and metaxylene (136° – 137°), in the ratio of 5 : 2 approximately showed a similar tendency to gather at 130° – 131° .

Amyl alcohol (128° – 129°) and brombenzene (152° – 153°), in the ratio of 5 : 2 approximately seemed to be distilled at 128° –

129°, but the small per cent. of the latter and the formation of tar prevented a definite determination.

Summary.—Of the 80 mixtures examined, 45 were distilled at a constant temperature at or below the boiling-point of the more volatile constituent; 2,¹ at a constant temperature above the boiling-point of the less volatile constituent; 1,² at a constant temperature between the boiling-points of the constituents; 1,³ in which the boiling-points of the constituents are too close for fractionation, presents no relative depression or elevation of the boiling-point of the mixture; and 3 are of an uncertain character.

BOILING-POINTS OF MIXTURES OF LIQUIDS WHOSE MUTUAL SOLUBILITIES ARE LIMITED.

Two cases of this kind were examined.

1. Isobutyl alcohol (105.3°–106.3°) saturated with water at the temperature of the room (about 5 parts of alcohol to 1 part of water) boils for a time at the constant temperature of 89°–90°, the distillate separating in the receiver into two layers. The excess of alcohol above the amount necessary for the proportions of distillation at constant temperature causes the temperature to rise gradually to 106°. If the alcohol be saturated at higher temperatures, the portion distilling at 89°–90° is correspondingly larger.

2. Methyl alcohol (64.5°–65°) saturated with carbon disulphide (45.5°–46°) (about equal parts by weight at the temperature of the room) boils for a time at 37°–38°. The excess of alcohol causes the temperature to rise ultimately to 65°. This mixture shows phenomena similar to those noted in case 1.

CONCLUSIONS.

1. The large proportion of constant boiling mixtures found in the cases examined makes it evident that this phenomenon is by no means so exceptional as has hitherto been supposed. In fractional distillation one should always be on his guard against it.

¹ Nos. 45 and 46.

² No. 48.

³ Ether-ethyl bromide.

2. The changes in the composition of the distillates, corresponding to the changes in pressure and temperature of the distillation, indicate that the two mixtures investigated¹ are not true chemical compounds, and that any approximation to molecular proportions must be regarded as accidental.

3. It is well known that two liquids mutually insoluble are distilled at a constant temperature in the ratio of the products of their respective vapor-densities and vapor-tensions at the temperature of distillation.

If the liquids are partially soluble in each other, they are also distilled at a constant temperature, but with some deviation from this ratio, so long as there are two layers of liquids in the distilling-flask.

The results of this investigation are generally in accord with the theory that when two liquids, mutually soluble in all proportions, are distilled at a constant temperature, their ratio in the distillate is that of the products of the vapor-densities and vapor-tensions of the pure liquids at that temperature, modified more or less by their influence upon each other.²

¹ See pages 9-10.

² The greatest deviation from the calculated ratio was found in the mixture of propyl alcohol and benzene (No. 22).

BIOGRAPHICAL SKETCH.

Garnett Ryland was born in King and Queen County, Virginia, December 17, 1870. He was prepared at McGuire's School in Richmond for Richmond College, from which he graduated in June, 1892, with the degree of Master of Arts. After teaching for three sessions, he entered the Johns Hopkins University in October, 1895, as a graduate student in chemistry, with physics and mathematics as subordinate studies.

